The Surface Structure of α-Fe_2O_3(0001) by Low Energy X-Ray Photoelectron Diffraction

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INTRODUCTION

The structure and composition of oxide surfaces strongly influence their chemical properties. As such, there is a growing interest in determining the surface termination, reconstruction and relaxation of these surfaces. There is a growing interest in iron oxide surfaces because of their importance in surface geochemistry, heterogeneous catalysis, magnetic recording and integrated microwave devices [1-4]. In a recent study [5] of the selective epitaxial growth of magnetite (Fe_3O_4) and hematite (α-Fe_2O_3), it was shown that the surface of (001) magnetite exhibits a ($\sqrt{2}$x $\sqrt{2}$)R45° reconstruction. The relaxation or contraction of first few layers hasn't been addressed in ref. 5 or any other studies in the literature. Recent theoretical work by Wasserman et. al [6] have shown that (0001) hematite has a single Fe layer termination with relaxations in the first four layers of -48%, -2%, -35%, and 21%, respectively. We recently performed low-energy x-ray photoelectron diffraction measurements at Advanced Light Source on a clean, epitaxially grown hematite(0001) surface. Low-energy photoelectron diffraction data, which are briefly described below, were used to determine the relaxation of the first four layers.

EXPERIMENT

Low-energy photoelectron diffraction experiments were carried out on beam line 9.3.2 at the ALS. The end station at this beam line is equipped with a Scienta SES 200 hemispherical analyzer for collection of photoelectron spectra, along with a five-axis sample manipulator and in situ sample cleaning capabilities. An epitaxially grown α-Fe_2O_3 film grown on a Al_2O_3(0001) substrate at PNNL was cleaned and ordered by annealing in oxygen at a pressure of $1x10^{-6}$ torr and a temperature of 900 K. A photon energy of 400 eV was used to collect several Fe 3p azimuthal scans at different take off angles. The Fe 3p kinetic energy was 344 eV. Although sample charging was neutralized by electrons from a hot filament which was housed close to the sample, it was impossible to get reliable low kinetic energy data for photon energies below 350 eV. The sample was cleaned and ordered at the start of each azimuthal scan and the cleanliness of the surface was checked before and after every scan. Approximately ≤ 0.15 monolayer of hydroxyl, adsorbed during the tranfer from PNNL to ALS, was always seen on the surface and the clean 1x1 LEED pattern indicates that there is no specific ordering of hydroxyl on the surface. Theoretical simulations were carried out using spherical wave single scattering cluster theory for select trial geometries [7] with the partial wave phase shifts being computed using the program FEFF [8]. The cluster size was about 950 atoms for the single scattering calculations.

RESULTS

Our ALS experimental results are summarized in Figs. 1 and 2. Fig. 1 shows the experimental and

theoretical azimuthal scans for take off angles of θ = 10°, 15° and 20°. The experimental and theoretical azimuthal scans for take off angles of θ = 26° and 32° are presented in Fig. 2. The theoretical scans are the photoelectron diffraction intensities simulated from an optimized single Fe

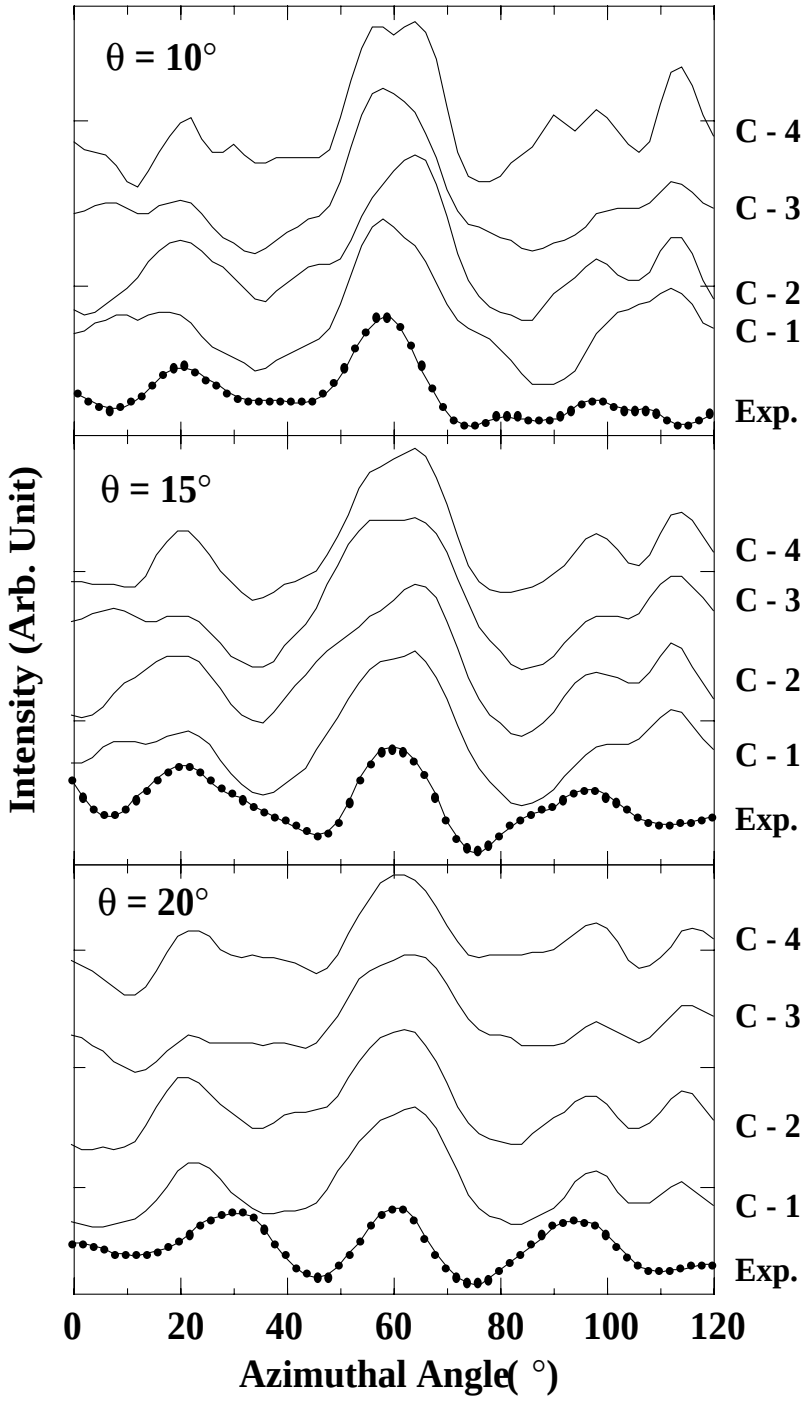

Fig. 1: Experimental and theoretical photoelectron diffraction intensities as a function of azimuthal angle for the take off angles, θ = 10°, 15°, and 20°; C-1 = optimized Fe-terminated cluster, C-2 = optimized O-terminated cluster, C-3 = cluster derived from the relaxations proposed by Wasserman et al.[6], and C-4 = C-3 with one monolayer of OH [6].

layer terminated surface (C-1), an optimized O layer terminated cluster (C-2), a relaxed single Fe layer terminated cluster(C-3), proposed by Wasserman et al. [6] and a relaxed single Fe terminated cluster with one monolayer of hydroxyl attached a top all the cation sites (C-4), proposed by Wasserman et al. [6]. Layer spacings were systematically varied between ±0.600 Å with 0.10 Å steps for these calculations and a detailed R-factor analysis was carried out. From the low take off angles data, especially for $\theta = 10°$, and 15° which are more surface sensitive, the misfit between the experimental intensities and the intensities calculated from the optimized O-terminated cluster (C-2) and Fe terminated cluster with one monolayer of hydroxyl (C-4) could be clearly seen. The main peak around the azimuthal angle range of 58°-60° appeared to be shifted by about 6-8° for C-2 and about 3-4° for C-4 respectively for the take off angles of 10° and 15°. These results confirm that the hematite surface is terminated by a single Fe layer. The R-factors for the five angles are summed and the average R-factor, R_1 (the other four R-Factors, R_2-R_5 vary as R_1) for optimized C-1 and C-2, proposed clusters C-3, and C-4 along with the layer spacings are given in Table I. The results from the R-Factor analysis also suggest that the surface is Fe-terminated. The differences of R-factors between the clusters are small since the kinetic energy of 344 eV is not completely surface sensitive. However, since the anisotropies of these scans vary between 30-40%, the change in R-Factors reflect the change in the geometry of the cluster.

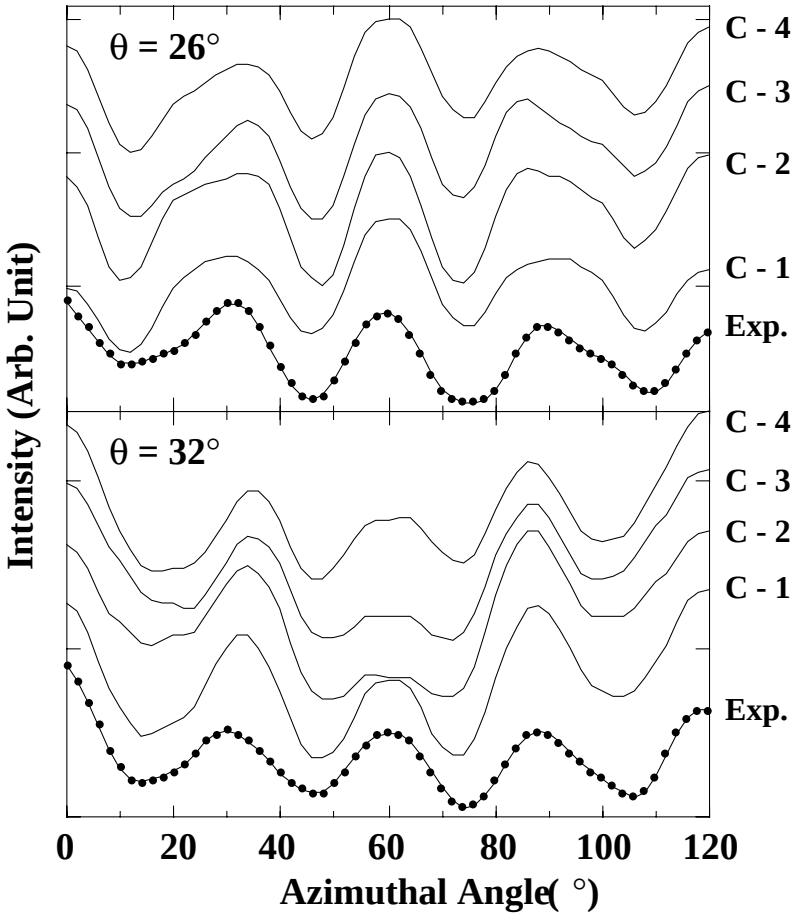

Fig. 2: Experimental and theoretical photoelectron diffraction intensities as a function of azimuthal angle for the take off angles, $\theta = 26°$, and 32°; C-1 = optimized Fe-terminated cluster, C-2 = optimized O-terminated cluster, C-3 = cluster derived from the relaxations proposed by Wasserman et al.[6], and C-4 = C-3 with one monolayer of OH [6].

TABLE I: The optimized layer spacings, and the average R_1 for four different clusters

Cluster	Layer 1 Fe-B=0.845Å O-B=0.845 Å	Layer 2 Fe-B=0.845Å O-B=0.605 Å	Layer 3 Fe-B=0.605Å O-B=0.845 Å	Layer 4 Fe-B=0.845Å O-B=0.845 Å	Average R_1
C-1 Fe-terminated	0.500 Å -41%	0.995 Å 18%	0.555 Å 8%	1.245 Å 47%	0.07625
C-2 O-terminated	1.195 Å 41%	0.605 Å 0%	0.745 Å -12%	0.795 Å -6%	0.07853
C-3 Fe-terminated Ref. 7	0.436 Å -48%	0.825 Å -2%	0.394 Å -35%	1.021 Å 21%	0.08519
C-4 Fe-term./OH Ref. 7	0.819 Å -3%	0.853 Å 1%	0.425 Å -30%	0.980 Å 16%	0.07738

CONCLUSIONS

In conclusion, we have used photoelectron diffraction to determine the surface structure of hematite (0001) surface. The surface appears to be Fe-terminated and the first four layer spacings are -41%, +18%, -8%, and 47% of the associated bulk values, respectively.

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